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The use of twin screw extruders as starch modification reactors.

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Chapter 11. Summary and conclusions

In general it can be concluded that twin screw extruders are very suitable starch modification reactors. High conversions, selectivities and substitution degrees can be obtained. Moreover, new innovative starch products can be made.

(De Aardappeleters, sketched in 1885 by Vincent van Gogh)

11.0. Summary and conclusions

11.1. Introduction

Starch is an important raw material that can be used in many industries varying from the food and adhesive to plastic manufacturing. Chemical and physical modification reactions have lead to the use of modified starches in a wide range of industrial applications. In order to maintain this position, continuous innovation of the processes and products is essential. In this thesis attention is given to some processes as well as to products [1]. Twin screw extruders can be used to produce modified starches continuously by which a more constant quality product is obtained. Moreover, the extruder has the advantage of good mixing of highly viscous fluids, enhanced heat transfer and good plug flow characteristics. Due to these advantages, high conversions and selectivities are obtained which can not be achieved using conventional reactors. Changing starch properties like the water resistance, the tensile and the impact strength, new starch products and thus new appliancations can be obtained.

11.2. Kinetics

In chapter 3 the kinetics of the reactions used were investigated. Only in the case of the hydroxypropylation and the acetylation of starch, the kinetics were important because the grafting of styrene on starch is a diffusion controlled process. Figure 11.1 presents an overview of the reaction rates of the main reactions tested versus the reaction temperature.

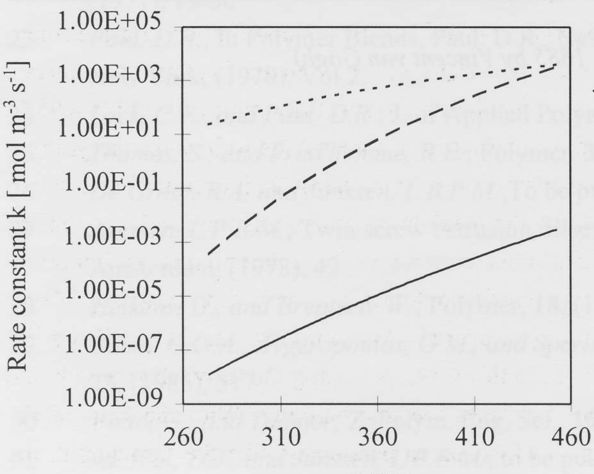

Fig. 11.1: *Reaction rates as a function of the temperature for three different reaction types Acetylation of starch Hydroxypropylation of starch*
— : *Hydroxypropylation*
– – : *Acetylation*
---- : *Styrene polymerisation*

The main differences between the two kinetic controlled reactions were the reaction velocity and the side reactions occurring. In the case of the hydroxypropylation, part of the reactant reacted with the catalyst in a parallel reaction or with the formed hydroxypropyl starch to di-hydroxypropylstarch. This last reaction could not be measured, but according to Lammers, *et al* [2] this reaction only takes place at molar substitution degrees (MS's) greater than 1, which was not attained in the used extruder equipment. Increasing the catalyst concentration, the temperature or the water concentration resulted in a decreasing selectivity. In the case of acetylation of starch, both a parallel base catalysed hydrolysis reaction of vinylacetate and a consecutive hydrolysis reactions of the formed end product occurs. The selectivity of the main reaction can be increased with increasing temperatures or starch concentrations.

11.3. Reactive extrusion results

11.3.1. Counterrotating twin screw extruder

An investigation of the reactive extrusion process in a counterrotating extruder was carried out with the acetylation of starch and the grafting of styrene on starch. Before reactions were performed in this extruder type, models were developed in order to understand the mixing behaviour and the reaction kinetics. The kinetics of the acetylation of starch were measured revealing that in order to obtain high conversions, selectivities and degree of substitutions (DS's), high temperatures and low water contents should be used. In the case of the grafting of styrene on starch the main parameters are the reaction temperature, the initiator concentration and the mixing between the water and the styrene phase.

In addition to the kinetic experiments, the residence time distribution and the micro mixing were measured and modelled. Assuming perfectly mixed C-shaped chambers a residence time model could be set-up predicting the first three moments within a 95 % accuracy. Models were developed for non-reacting materials as well as for the grafting of styrene on starch. From the models and from measurements it appeared that due to the higher density of the end product, the breakthrough time and the residence time of reacting material increased. Besides macromixing also micromixing is important when multi-component reactions are carried out. Using a method proposed by Meyer *et al.,* [3], this micromixing was measured. Micromixing trends predicted by Ganzeveld *et al.,* [4] were quantified in this way. Increasing the fully filled length, the screw speed or the die resistance increases the micromixing. With the help of the models mentioned above, the effect of extrusion parameters like the throughput, the barrel temperature, the die resistance and the screw rotation rate on the product were analysed. In the case of the acetylation reaction high DS's (0 - 0.25) and conversions (100 %) could be attained. In order to obtain high DS's complete gelatinised starch should be used which can be obtained by using a high shear screw geometry.

In the case of the diffusion limited reaction of styrene with starch, mixing is the main parameter. Increasing the mixing by increasing the fully filled length and the screw speed, gives higher grafting percentages and conversions. Using a co-monomer like MAH or a different initiator (BPO) the reaction parameters mentioned above also increased due to an increased reaction temperature. In this way the graft percentage, the molar masses and the amount of homopolymer formed can be controlled. The molar mass was also controlled by adding a chain transfer agent.

11.3.2. Selfwiping twin screw extruder

An investigation of the reactive extrusion process in a selfwiping extruder was carried out with the slow reaction of starch with propylene oxide forming hydroxypropylated starch. Before the reaction was performed in this extruder type, models were set-up in order to understand the mixing behaviour and the reaction kinetics. The kinetic of this reaction showed that in order to obtain high conversion, selectivities and MS values; low water concentrations should be used. High temperature lowers the selectivity but increases the conversion. The same mechanism occurs when the alkali amount (catalyst) is increased.

Also the micromixing and the residence time distribution of this extruder were examined. Assuming a plug flow characteristic the residence time distribution could be modelled, predicting the first three moments within 1 % of the measured values. The micromixing occurring was measured using a perspex extruder. Results opposite to what was expected were obtained in the case of large viscosity ratios. Until now no good explanation for this phenomenon can be given.

With the help of the models mentioned above, the effect of extrusion parameters like the throughput, the barrel temperature, the die resistance and the screw rotation rate on the reaction of propylene oxide with starch was analysed. This relative slow reaction in a selfwiping extruder gave conversions of 100 %, selectivities of > 70 % and DS's ranging from 0 to 0.45. With the help of the model presented in chapter 9 a good understanding of which parameters determine the extrusion process was obtained. Both model and measurements showed that the viscosity change of the processed material is very important in this type of extruder. The change of the starch viscosity as a function of shear, temperature and substitution degree is considerable, giving rise to all kinds of side effects. These effects operate at the same scale but also influence each other, making it difficult to predict which parameter is at a certain point the most important. Using an extrusion interaction diagram is in this case helpful to understand qualitatively the effects. In order to obtain quantitative results, models as mentioned in chapter 9 should be used.

11.4. New plastics made of biodegradable starch materials

Mechanical blending of two or more incompatible polymers promises new materials with specific properties. In this study two blends were compared namely: PS blended with PS-g-Starch and blends made of PS, starch and PS-g-starch. Material properties like biodegradability, impact strength and tensile strength could be changed easily by varying, for instance, the graft percentage or the molar mass. In this way a whole range of materials can be produced with tailor made properties.
Based on theories of deformation and breakup processes of droplets in well-defined flow fields, the final droplet diameter in blends can be predicted. Comparison of these theoretical results for two incompatible (non-equilibrium) polymers with TEM pictures from the blends of PS, starch and PS-g-Starch, shows that the dispersion of droplets is reduced by a factor 10. In this way polymers can be obtained with a fine scale morphology.

11.5. References

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